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Raman Scattering from Tin

by Patrick A Folkes, Patrick Taylor, Charles Rong,
Barbara Nichols, Harry Hier, and Mikella Farrell

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Sensors and Electron Devices Directorate, ARL

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1. Introduction

We are doing research on materials and processing that will enable us to investigate the unique electronic states between topological insulators (TIs) and high-temperature superconductors. TIs are electronic materials that have a bulk bandgap and gapless conducting surface states that are protected by the topological and symmetry characteristics of their bandstructure.¹ One of the fundamental characteristics of TIs is the occurrence of gapless surface states where the conduction band and the valence band touch each other at distinct points in the Brillouin zone called Dirac points. Near those points the electronic energy-momentum dispersion is similar to the linear dispersion of massless relativistic electrons described by the Dirac equation.¹ TIs exhibit spin-filtered ballistic transport in edge channels where the up-spins propagate in one direction, while the down-spins propagate in the opposite direction at low temperatures and elastic backscattering is suppressed in the absence of magnetic impurities. These results suggest the possible realization of room-temperature electrical conduction without dissipation in the edge channels of 2-dimensional (2D) TIs with a large bandgap and applications in TI-based energy efficient devices.² However, the small bulk bandgap in existing 2D TIs limits their potential application in electronic devices. Recent theory³ has predicted that 2D tin films (stanene) are 2D TIs with a bulk bandgap up to 0.3 eV, which is sufficiently large for practical applications at room temperature. The 2D tin topological surface states can be effectively tuned by chemical functionalization. This theoretical prediction has not been observed because growth of the 2D tin film has not been achieved.

One new material we are investigating is stanene, the 2D monolayer of elemental tin (Sn) that has a hexagonal (honeycomb) lattice. Bulk single-crystal tin is a 0-bandgap semiconductor (α -Sn) that is stable at temperatures lower than 286 K and undergoes a phase transition at 286 K to metallic tin (β -Sn), the stable tin allotrope at temperatures above 286 K.⁴ High-quality single-crystal layers of α -Sn that are less than 0.5 μm thick can be grown by molecular beam epitaxy (MBE)⁵ on indium antimonide (InSb) substrates at room temperature. The transition of MBE-grown layers of semiconducting α -Sn to metallic β -Sn occurs at around 390 K.⁶ The phase transition from bulk metallic β -Sn to semiconductor α -Sn can occur by cooling β -Sn below 150 K for an extended period of time.⁷ This phase transition is accompanied by a change in color of the white β -Sn to gray α -Sn, a 27% increase in volume leading to powdery α -Sn or a highly strained α -Sn with a lot of cracks.⁶

We plan to do the MBE growth of stanene at around 286 K using substrates that have very few surface dangling bonds and are known to promote van der Waals

epitaxial growth of hexagonal single monolayers even with highly lattice-mismatched materials. The potential for producing stanene is believed to be improved by key substrate criteria: 1) a non-chemically-interacting substrate and 2) (111) crystal symmetry. Several different non-chemically bonding substrates with (111) symmetry will be utilized in this research on the growth of stanene. These are freshly cleaved barium fluoride (BaF_2), crystalline-silicon dioxide (SiO_2), molybdenum disulfide (MoS_2), and single crystal hexagonal boron nitride (BN). The role of these substrates will be to induce hexagonal arrangement of Sn on the surface, while promoting the preferential bonding of Sn to itself instead of the substrate. Raman scattering will be used to characterize the Sn film and study the dependence of the Raman characteristics on the thickness of the Sn and its thermal stability. Raman scattering in single-crystal and polycrystalline Sn has been reported.^{8,9} Because very little experimental and theoretical work on Raman scattering from Sn has been done, it is imperative that we study the Raman scattering from bulk metallic and semiconductor tin as well as MBE-grown layers of Sn. This could lead to the use of Raman scattering for the characterization of single-layer and few-layer stanene films.

2. Experimental

An electron beam deposition system was used to deposit polycrystalline Sn layers as a step toward the MBE growth of stanene. We deposited 99.9999% pure tin metal with a thickness of around 10 nm on freshly cleaved BaF_2 single-crystal samples, as well single-crystal z-cut SiO_2 $\frac{1}{4}$ -wafers. The obtained Sn layers on all substrates were opaque, but highly specular and featureless, as shown in Fig. 1.

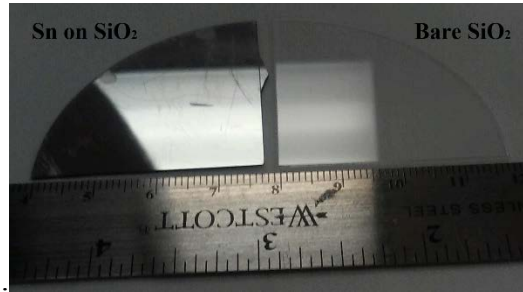


Fig. 1 Image of tin layer on $\frac{1}{4}$ -wafer of SiO_2 (left) and bare $\frac{1}{4}$ -wafer of SiO_2 (right)

The as-deposited phase of Sn appeared to be the metallic (β) phase tin; however, the structure could easily be transformed to the sp^3 -bonded semiconductor phase (α -Sn) by cooling to 77 K for 2–4 h. The thickness of the deposited samples was chosen to facilitate characterization and understanding, so in future work, we plan to reduce the thickness of the Sn layer to sub-monolayer. A Witec alpha 300a

spectrometer was used to detect the Raman scattering spectra with a resolution of 0.9 cm^{-1} at 300 K in the back-scattering geometry using a 1 mW, 532 nm laser. Raman spectra were obtained from the bare BaF_2 , the bare SiO_2 , the polycrystalline as-deposited metallic Sn/BaF_2 and Sn/SiO_2 samples, and high-purity polycrystalline Sn lumps. After immersion in liquid nitrogen for 2.5 h, the metallic Sn on the substrates and the Sn lumps appear to have undergone at least a partial phase transition to the semiconductor tin phase as evidenced by a change in color and morphology. Raman scattering measurements were repeated on the converted semiconductor Sn samples.

3. Results

The Raman spectrum from BaF_2 shown in Fig. 2, shows a single narrow Raman peak from BaF_2 at 243 cm^{-1} . The Raman signal from high-purity Sn that was deposited on a BaF_2 substrate is shown in Fig. 3. The oxide peaks at 89 and 132 cm^{-1} from the unpassivated Sn are quite broad and there is a large background signal from diffuse Raleigh scattering from the surface. These effects combine and result in a poorly resolved Raman peak from Sn at 200 cm^{-1} . This data clearly indicates the need for future passivation of stanene. Figure 3 shows that the BaF_2 beneath the Sn can be resolved in the Raman scattering spectrum. The clean BaF_2 Raman spectrum, the fact that it can be MBE-grown in-situ and its inert chemical characteristics indicate that BaF_2 is an excellent passivation layer for stanene. In contrast, Figs. 4 and 5 show that the Raman spectrum of SiO_2 has multiple peaks, which make it much more difficult to resolve the Sn peak in the Raman spectrum of Sn deposited on SiO_2 .

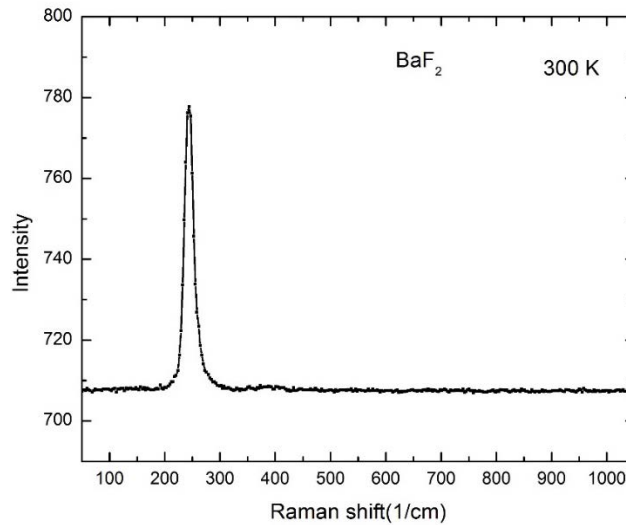


Fig. 2 Raman spectrum from the BaF_2 substrate

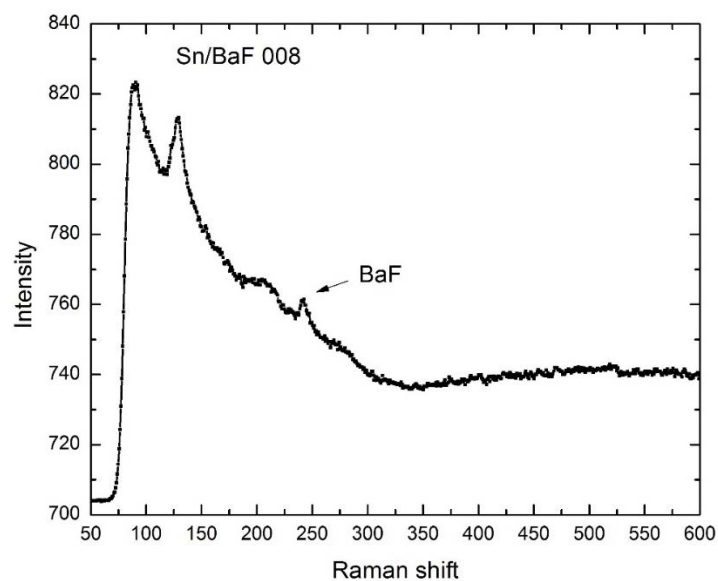


Fig. 3 Raman spectrum from deposited Sn on the BaF₂ substrate

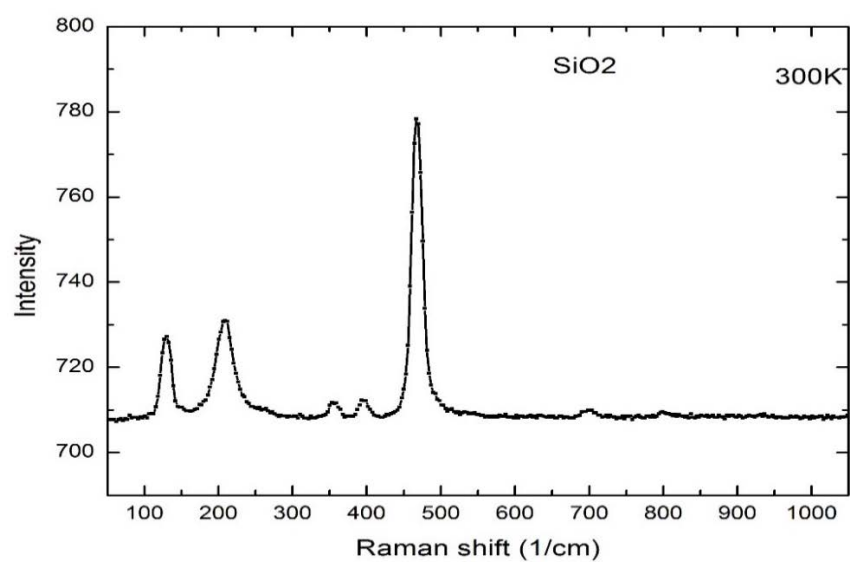


Fig. 4 Raman spectrum from SiO₂

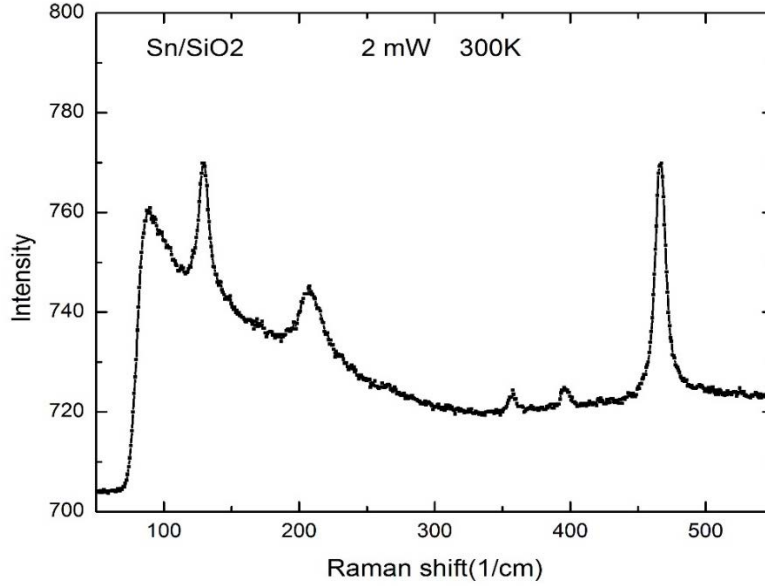


Fig. 5 Raman spectrum from tin deposited on SiO₂

Figure 6 shows Raman scattering from a high-purity polycrystalline metallic Sn lump at 300 K. The Raman scattering from metallic tin has peak at 218.5 cm^{-1} possibly indicating that this Sn lump is highly strained. To our knowledge, this is the first measurement of first-order Raman scattering from metallic Sn. Further research is needed to confirm this. The plot shows a prominent Raman peak the surface oxide at around 131 cm^{-1} . After being immersed in liquid nitrogen for 2.5 h, the metallic Sn sample appears to have undergone a phase transition to the semiconductor phase as evidenced by a change in color. The first-order Raman scattering signals from semiconductor tin at various temperatures are shown in Figs. 7–9. The Raman peak from semiconductor Sn at around 150 and 300 K occurs at 209.7 and 211.4 cm^{-1} , respectively. Note that the Raman scattering signal from the semiconductor Sn lump is smaller partly due to optical alignment and much broader than the signal from metallic Sn lump.

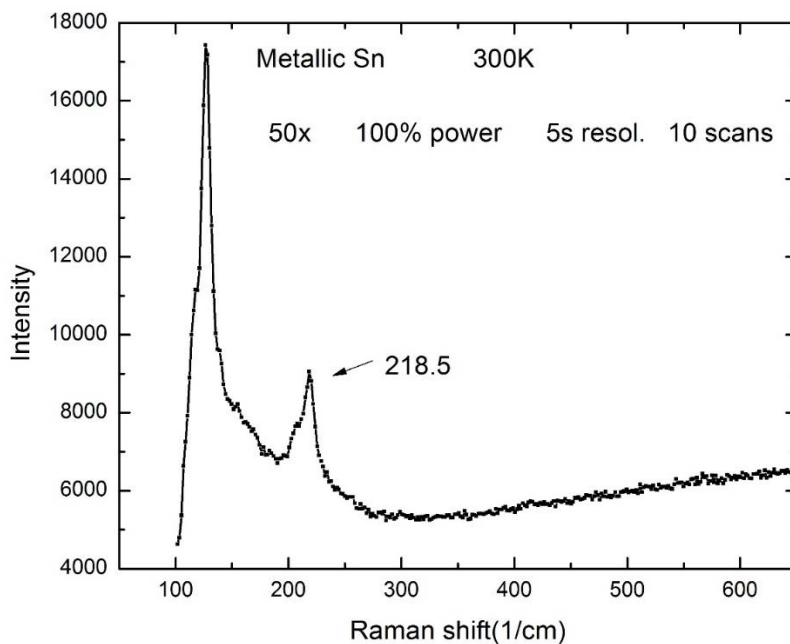


Fig. 6 Raman spectrum from the metallic Sn lump at 300 K

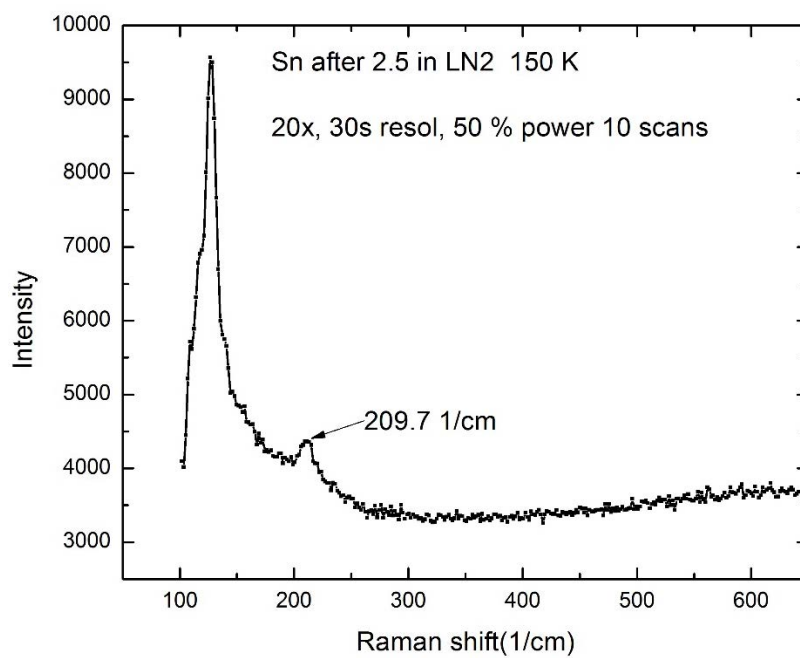


Fig. 7 Raman spectrum from the semiconductor Sn lump at 150 K

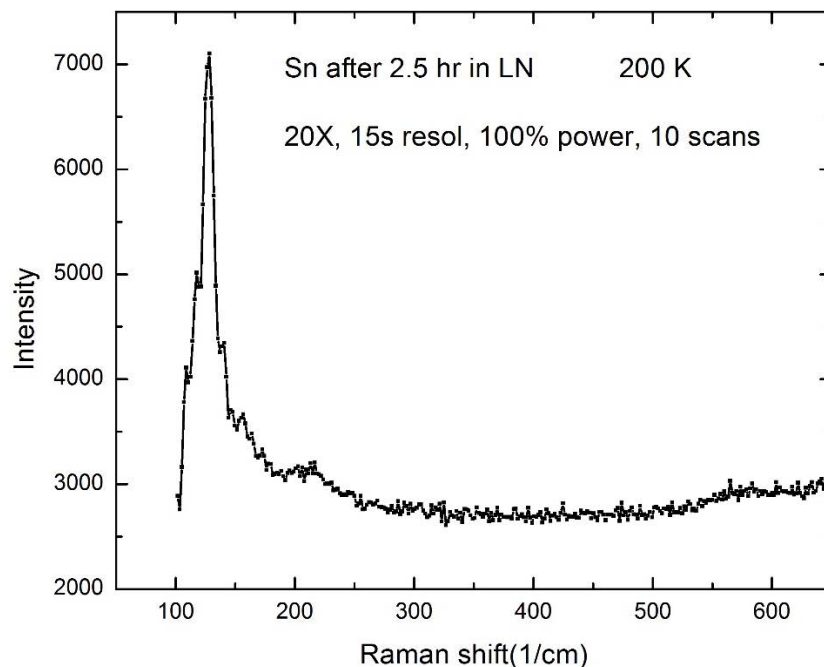


Fig. 8 Raman spectrum from the semiconductor Sn lump at 200 K

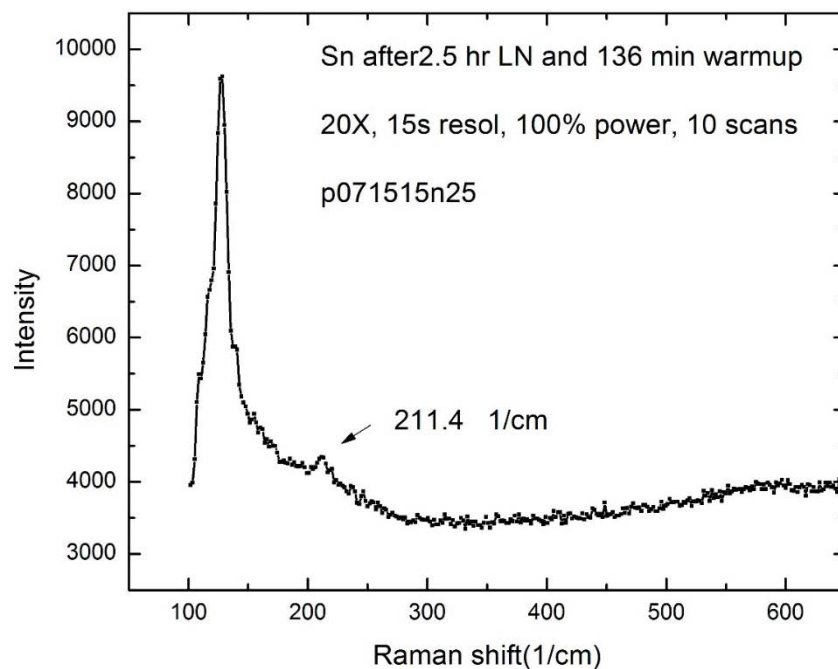


Fig. 9 Raman spectrum from the semiconductor Sn lump at 300 K

4. Conclusion

Along the path toward realizing the MBE growth of stanene, we have shown 2 accomplishments: 1) we have new processes to deposit ultra-thin (<10 nm) Sn

layers on the substrates of interest and 2) we have used Raman spectroscopy of Sn as an analytical tool for discerning specific allotropic differences in ultra-thin Sn films, and discerning differences between the Sn and the substrates of interest. We have acquired spectra from BaF₂, crystalline SiO₂, as well as ultra-thin Sn semiconductor and Sn metallic allotropes, and we are developing a fundamental understanding of the spectra. The research has identified that BaF₂ is an excellent passivation layer for stanene that will enhance the resolution of the Raman spectrum of future Sn layers and facilitate the MBE growth of stanene.

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List of Symbols, Abbreviations, and Acronyms

2D	2-dimensional
BaF ₂	barium fluoride
BN	boron nitride
InSb	indium antimonide
MBE	molecular beam epitaxy
MoS ₂	molybdenum disulfide
SiO ₂	silicon dioxide
Sn	tin
TIs	topological insulators

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